

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

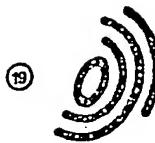
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 351 208
A2

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 89307073.0

⑮ Int. Cl. 5: C 08 F 8/50
C 08 L 23/02

⑭ Date of filing: 12.07.89

⑯ Priority: 15.07.88 US 219681

⑰ Date of publication of application:
17.01.90 Bulletin 90/03

⑲ Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

⑳ Applicant: EXXON CHEMICAL PATENTS INC.
200 Park Avenue
Florham Park New Jersey 07932 (US)

㉑ Inventor: Randall, James Carlton
Marnixlaan 64
B-1900 Overijse (BE)

Huff, Terence
5101 Inverness
Baytown Texas 77521 (US)

㉒ Representative: Dew, Melvyn John et al
Exxon Chemical Limited Exxon Chemical Technology
Centre P.O. Box 1
Abingdon Oxfordshire, OX13 6BB (GB)

㉓ Impact modified polymers.

㉔ Impact-modified polymeric materials are produced by visbreaking certain reactor blends. In a preferred embodiment, impact-modified polypropylene materials are produced by visbreaking a reactor blend of polypropylene and thermoplastic polyethylene. The polypropylene material is preferably homo-polypropylene having a melt flow rate of less than about 1 dg/min. Such impact-modified polymeric materials manifest unexpected compatibility characteristics, increased impact-resistance at low temperatures, improved antiblush characteristics and improved flow characteristics.

EP 0 351 208 A2

Description

IMPACT-MODIFIED POLYMERS

The present invention relates to polymeric materials, preferably polypropylene based polymeric materials, having improved impact resistance and, more particularly, relates to visbroken reactor blends of free radical crosslinkable thermoplastic olefin polymers, such as thermoplastic polyethylene materials, and free radical decomposable olefin polymers, such as polypropylene materials, preferably high molecular weight polypropylene materials. The visbroken reactor blends of the present invention manifest high resistance to impact at low temperatures and have excellent stiffness and flow characteristics. Most importantly, the subject visbroken reactor blends comprise a continuous olefin polymeric phase and a dispersed thermoplastic olefin polymeric phase wherein improved adhesion characteristics are achieved between the dispersed and continuous phases, due in part to the presence of grafts. The grafts comprise a portion of free radical decomposable olefin polymer fragmented, or visbroken, material grafted to a portion of the free radical crosslinkable thermoplastic material. These grafts serve as compatibilizers or surface active agents between the phases. In a preferred embodiment, the free radical decomposable olefin polymer is polypropylene and the free crosslinkable thermoplastic olefin polymer is polyethylene. Preferably, the polypropylene material utilized is a high molecular weight material so that more polypropylene fragments are available for grafting and a larger amount of surface active grafts are thus provided to improve adhesion between the dispersed and continuous phases. The visbroken reactor blends of the present invention are particularly characterized by the fact that they do not include rubber materials yet manifest significantly improved low temperature impact resistance while maintaining excellent stiffness characteristics.

The present invention resides in the discovery that improved impact-modified polypropylenes are obtained by visbreaking a reactor blend of polypropylene and thermoplastic polyethylene. Polypropylene is known to be deficient in resistance to impact at low temperatures, i.e., 5°C and below. Polypropylene materials which have been modified to improve resistance to impact are generally referred to as impact-modified polypropylenes. Heretofore, impact resistance of polypropylene has been improved by blending impact resistant materials such as elastomeric ethylene-propylene copolymers therewith or by reacting therewith other polymers or copolymers to produce reactor blends typically referred to as impact copolymers. There is, however, a tradeoff with other properties, e.g., stiffness and flow characteristics, when such polypropylene materials are impact-modified. For example, U.S. Patent No. 4,459,385 discloses that impact-modified polypropylenes obtained by sequential polymerization of propylene, and ethylene and propylene, to obtain an impact copolymer of polypropylene homopolymer and elastomeric ethylene-propylene copolymer, while having good impact resistance at low temperatures, have decreased stiffness. This reference teaches that as a general rule, impact resistance increases and stiffness decreases with increasing amounts of elastomer in the total composition. Such patent also discloses that the decrease in stiffness can be compensated for by blending with the impact-modified material a linear low density polyethylene (LLDPE) having a melt flow index not exceeding 5 dg/min. U.S. Patent No. 4,535,125 discloses that impact-modified polypropylenes blended with a LLDPE have poor flow performance and that such flow performance is improved through visbreaking. That is, the melt flow rate of the blend of impact copolymer and LLDPE can be increased by extruding the blend in the presence of certain peroxide materials. Thus, impact-modified polypropylenes are blended with a LLDPE having a melt flow index of from 5 to 50 dg/min and the blends are visbroken to obtain impact-resistant polypropylene materials which have good stiffness characteristics as well as good flow characteristics.

Other methods of preparing impact-modified polypropylenes are also known. For example, U.S. Patent No. 4,375,531 discloses blends of a first component selected from a group of medium impact polymeric materials with a second component selected from a group of high impact polymeric materials which blends are visbroken to improve the flow characteristics thereof.

It can be seen from the prior art that impact resistant polypropylenes having good flow and stiffness characteristics are prepared starting with polypropylene materials which have already been impact-modified, i.e., contain elastomers and the like, and blending therewith another material such as LLDPE to improve the stiffness characteristics of the impact-modified polypropylene followed by visbreaking the blend to improve the flow characteristics of the blend. However, such products manifest an undesirable balance between impact resistance and stiffness. Furthermore, products produced from such materials exhibit "blushing" or "stress whitening" upon impact which gives an appearance of a defective product.

It has now been discovered that, contrary to the teachings of the prior art, high-impact resistant polypropylene materials which do not contain rubber materials, such as ethylene-propylene rubber, and which do not contain stiffness modifiers, such as LLDPE, yet have excellent flow and stiffness characteristics as well as superior antiblush characteristics, are obtained by visbreaking reactor blends of thermoplastic polyethylene and polypropylene materials preferably prepared in the absence, or essential absence, of chain transfer agents such as hydrogen. That is, by restricting the flow of hydrogen, or other chain transfer agents typically utilized to control melt flow rate during sequential polymerizations, and subsequently visbreaking the reactor blended copolymers or sequentially polymerized copolymers, impact resistant polypropylene materials having superior impact resistance, stiffness and antiblush characteristics can be produced without adding an impact modifying component such as EP rubber.

Accordingly, the subject invention provides high impact resistant visbroken reactor blends suitable for use

in various applications, such as in molded products, wherein the products produced are significantly superior than those of the prior art. In addition, the improved impact-modified polymers of this invention are prepared in a more convenient manner and at a substantial cost saving as compared to the prior art materials.

In summary, this invention is directed to impact-modified polymers comprising visbroken reactor blends of free radical decomposable olefin polymers and free radical crosslinkable thermoplastic olefin polymers. In a preferred embodiment, the impact-modified polymer is impact-modified polypropylene obtained by visbreaking a reactor blend of polypropylene and thermoplastic polyethylene materials. The impact-modified polymers exhibit high impact resistance at low temperatures and have excellent flow, stiffness and antiblush characteristics. Furthermore, these impact-modified polymers manifest unexpected compatibility characteristics.

The present invention resides in the discovery that improved impact-modified polypropylenes can be obtained from certain visbroken reactor blends. The certain visbroken reactor blends are those reactor blends of thermoplastic polyethylene materials and polypropylene materials having at least about 90 wt.% propylene. Such materials are preferably prepared essentially in the absence of chain terminating agents such as hydrogen. Thus, the impact copolymers of the present invention are characterized by low melt flow rates prior to visbreaking. The visbreaking process can then be utilized to obtain a product having a desired melt flow rate. By "essentially in the absence of chain terminating agents" it is meant that the flow of such agents is restricted during the sequential polymerization process to that which is necessary to produce a polymer material which is adapted to be melt blended during the visbreaking process.

Typically, reactor blend materials are prepared utilizing significant amounts of hydrogen or other chain terminating agents in order to control the melt flow rate of both intermediates, e.g. homopolymer made in the first reactor and copolymer made in the second reactor, so that the reactor blend product is of a melt flow rate such as to permit processing in commercial applications.

By contrast, in the present invention, the flow of chain terminating agents, such as hydrogen, is restricted with the effect that the resulting reactor blend has a low melt flow rate, i.e., high molecular weight. Upon visbreaking of the low melt flow rate blend, i.e., high molecular weight material, the number of fragments of reactor blend material can be controlled to produce a product having a desired melt flow rate. More importantly, the number of grafts and blocks, as discussed below, can now be controlled in order to facilitate control of impact strength, stiffness and antiblushing. Accordingly, the present invention is directed to impact-modified polypropylene compositions having excellent stiffness and flow characteristics as well as superior antiblushing characteristics.

In accordance with the present invention, there is provided a high impact polypropylene which comprises a reactor blend of polypropylene, preferably substantially isotactic high molecular weight homopolypropylene, and a thermoplastic polyethylene material, wherein the continuous phase of the reactor blend is the polypropylene and the dispersed phase is the polyethylene material.

By reactor blend, it is meant an in situ blend produced by polymerizing one or more monomers in the presence of another polymer, with at least some living catalyst being present during the polymerization. The resulting reactor product is a highly dispersed blend of the various polymers in which the components are mechanically inseparable.

The polypropylene material may comprise homopolypropylene or a copolymer of propylene with minor amounts of other comonomers, preferably one or more of C₂ or C₄ to C₁₀ alpha-olefins. Such minor amounts include amounts of up to about 10 wt.%.

The polyethylene may comprise homopolyethylene or a copolymer of ethylene with minor amounts of one or more other comonomers, preferably one or more of C₃ to C₁₀ alpha-olefins. The comonomer is present in the polyethylene in minor amounts of up to about 10% by weight, with more preferred ranges described below.

The high impact polypropylene of the present invention is produced in a series reactor system, either continuously or batchwise. Preferably, a substantially isotactic homopolypropylene is produced in a first reactor and the thermoplastic polyethylene is produced in a second reactor in the presence of the outlet stream from the first reactor. As a final step, the reactor blend from the second reactor is preferably melt admixed with an organic peroxide in effective amounts and under conditions to improve impact resistance of the reactor blend, particularly at low temperatures.

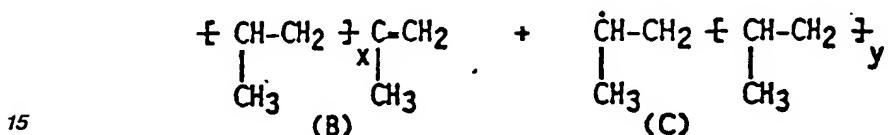
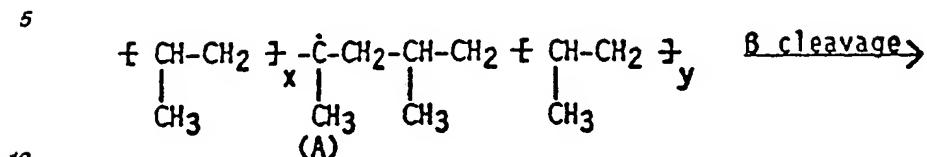
High impact polypropylenes in accordance with the present invention offer numerous advantages over conventional polypropylenes, including a more desirable stiffness/impact balance and improved resistance to stress whitening.

The high impact polypropylenes of the present invention are especially suited for use in molding applications to produce battery cases, automotive trim and the like.

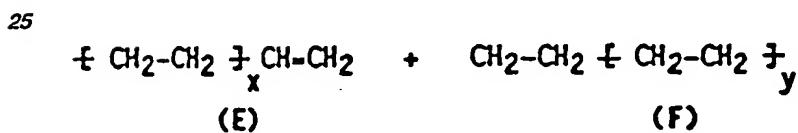
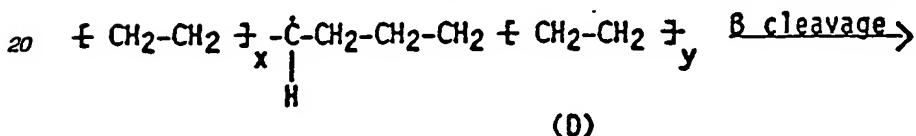
The high impact polymers of the present invention comprise a visbroken reactor blend of a continuous phase comprising a free radical decomposable olefin polymer, such as a polypropylene material, preferably, of high molecular weight, most preferably, a high molecular weight substantially isotactic homopolypropylene, and a dispersed phase comprising a free radical crosslinkable thermoplastic olefin polymer, such as a thermoplastic polyethylene material, preferably a thermoplastic ethylene copolymer.

Reactor blend, as that term is used herein, refers to a highly dispersed and mechanically inseparable blend of various polymers produced in situ as a result of the sequential polymerization of one or more monomers in the presence of a first polymer including some live catalyst from the first polymerization, with the formation of a second polymer in the presence of this first polymer.

(1) Polypropylene portion of reactor blend + ROO[•]
(peroxide) →



(2) Polyethylene portion of reactor blend + ROO[•] →



30 Reactions (1) and (2) are typically referred to as scission reactions and compete with another reaction referred to as linking (e.g., cross-linking of polyethylene). In the case of polypropylene, the scission reaction is thermodynamically preferred. Thus, polypropylene can be described as a free radical decomposable olefin. In the case of polyethylene, the linking reaction is preferred. Thus, the polyethylene can be described as a free radical crosslinkable olefin, and, in the present invention is a crosslinkable olefin plastic. Copolymers of 35 ethylene and another monomer also undergo the linking reaction, although in certain instances, may undergo the scission reaction, depending on the amount of comonomer. In addition to the fragments illustrated above, block and graft copolymers would be expected to be formed as well by radical combination (i.e., linking) of radical C with radicals D or F. Certain ones of these particular fragments, which include varying amounts of 40 propylene and ethylene, may prefer the scission reaction and others the linking reaction. The present invention is therefore directed to visbroken reactor blends of a free radical decomposable olefin and a free radical crosslinkable thermoplastic olefin.

45 Furthermore, although fragments (A) and (D) or (E) are the predominant fragment species, all of these fragments will be present at any given time and will eventually combine in varying arrangements to produce block or graft materials, the presence of which affects the reactor blend to modify certain physical characteristics thereof, such as impact resistance and stiffness.

50 In the present invention, which preferably involves low MFR, i.e., high molecular weight, homopolypropylene, more polypropylene fragments are necessarily produced to create the desired melt flow rate. Thus, an increased number of scission reactions occurs which leads to an increase in the number of grafts which in turn leads to an increase in impact resistance of the reactor blend.

55 Thus, the high impact polypropylene produced according to the teachings of the present invention can be tailored to have wide ranging physical properties suitable for a variety of applications without the addition of rubber. For example, for applications that require high stiffness and medium impact strength (i.e., battery cases and automotive interior trim) one might choose to produce a product with an essentially linear high density PE included or dispersed phase of high molecular weight product which on peroxide treatment, in the melt, would give the desired combination; conversely, if a product of very high impact strength but more modest stiffness is desired (i.e., luggage cases) one would choose a polyethylene included phase having a higher level of comonomer which on peroxide treatment would give the highest level of low temperature impact strength (although at some cost in reduced flexural modulus).

60 The foregoing more general discussion of this invention will be further exemplified by the following specific examples offered by way of illustration and not limitation of the above-described invention.

Examples:

65 In the following examples, mechanical property evaluations were made employing the following tests:

(1) Melt Flow Rate—ASTM D-1238, Condition L

(2) Flexural Modulus, secant--ASTM D-790.
 (3) Notched Izod Impact--ASTM D-256.
 (4) Gardner Impact--ASTM D-3029, Procedure B.

Example 1:

To a nitrogen purged 2 liter reactor fitted with a stirrer, the blades of which are a close fit to the reactor wall, there was introduced 4 ml of 0.1 molar diphenyldimethoxysilane in hexane, 4 ml of 1.0 molar triethylaluminum in hexane and 1250 ml of propylene. The reactor was brought to 70°C and 352 mg of a 30% white oil slurry of a commercial titanium chloride supported catalyst (trade designation TK-20, available from Mitsui Petrochemical Industries, Ltd., of Tokyo, Japan) was added. The polymerization was allowed to proceed for 45 minutes after which the temperature was rapidly lowered to 35°C and the reactor was vented of the unused propylene.

The vented reactor was tilted at a 45° angle and a gaseous flow of 100 mole% ethylene was introduced at a rate of 3.5 l/min. The reactor was maintained at 70°C and 0.69 MPa g (100 psig) pressure of the gaseous reactants. Constant pressure was maintained by continuous venting of the excess reactants. The polymerization was allowed to proceed for 30 minutes after which the reactor was cooled to 35°C and depressurized.

The polymer product was then recovered, dried, admixed with 1600 ppm of a 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (commercial designation Lupersol 101, available from the Lucidol Division of the Penwalt Corp., Buffalo, N.Y.) as a 50/50 wt/wt solution in Sontex 350 white oil, and extruded in a Killron 2.54 cm. (1 inch) single screw extruder (serial #5246) at 232°C (450°F) to yield a pelletized product. The pelletized product was compression molded in a Wabash 30 ton hydraulic press (Model No. 30-1515-2T2WCMB) to 0.38 cm. (0.125 inch) thick plaques from which appropriate test specimens were die cut. The test results are presented in Table I.

Comparative Example 1

The procedure set forth above in Example 1 was repeated in its entirety except for the following changes: (a) 0.17 MPa g (25 psig) of hydrogen was introduced into the liquid phase polymerization; (b) 355 mg of the 30wt% white oil slurry of the catalyst was utilized; and (c) no Lupersol 101 was added to the dried product.

The results are presented in Table I.

Example 2:

The procedure set forth above in Example 1 was repeated in its entirety except for the following changes: (a) 384 mg of the 30wt% white oil slurry of the catalyst was utilized; (b) a gaseous flow of 71 mole% ethylene and 29 mole% propylene was utilized as the feedstock to the gas phase polymerization; and (c) the dried product was admixed with 1273 ppm of Lupersol 101.

The results are presented in Table I.

Comparative Example 2

The procedure set forth above in Example 1 was repeated in its entirety except for the following changes: (a) 0.17 MPa g (25 psig) of hydrogen was introduced into the liquid phase polymerization; (b) 345 mg of the 30wt% white oil slurry of the catalyst was utilized; (c) a gaseous flow of 71 mole% ethylene and 29 mole% propylene was utilized as the feedstock to the gas phase polymerization; and (d) no Lupersol 101 was added to the dried product.

The results are presented in Table I.

Example 3:

The procedure set forth above in Example 1 was repeated in its entirety except for the following changes: (a) 362 mg of the 30wt% white oil slurry of the catalyst was utilized; (b) a gaseous flow of 97 mole% ethylene and 3 mole% hydrogen was utilized as the feedstock to the gas phase polymerization; and (c) the dried product was admixed with 1630 ppm of Lupersol 101.

The results are presented in Table I.

Comparative Example 3

The procedure set forth above in Example 1 was repeated in its entirety except for the following changes: (a) 0.17 MPa g (25 psig) hydrogen was introduced into the liquid phase polymerization; (b) 362 mg of the 30wt% white oil slurry of the catalyst was utilized; (c) a gaseous flow of 97 mole% ethylene and 3 mole% hydrogen was utilized as the feedstock to the gas phase polymerization; and (d) no Lupersol 101 was added to the dried product.

The results are presented in Table I.

Example 4:

The procedure set forth above in Example 1 was repeated in its entirety except for the following changes: (a) 346 mg of the 30wt% white oil slurry of the catalyst was utilized; (b) a gaseous flow of 68.9 mole% ethylene, 29 mole% propylene and 2.1 mole% hydrogen was utilized as the feedstock to the gas phase polymerization; and (c) the dried product was admixed with 1406 ppm of Lupersol 101.

5

10

15

20

25

30

35

40

45

50

55

60

65

The results are presented in Table I.

Comparative Example 4:

5 The procedure set forth above in Example 1 was repeated in its entirety except for the following changes: (a) 0.17 MPa g (25 psig) of hydrogen was introduced into the liquid phase polymerization; (b) 346 mg of the 30wt% white oil slurry of the catalyst was utilized; (c) a gaseous flow of 68.9 mole% ethylene, 29 mole% propylene and 2.1 mole% hydrogen was utilized as the feedstock to the gas phase polymerization; and (d) no Lupersol 101 was added to the dried product.

10 The results are presented in Table I.

Example 5:

15 The procedure set forth above in Example 1 was repeated in its entirety except for the following changes: (a) 466 mg of the 30 wt% white oil slurry of the catalyst was utilized; (b) a gaseous flow of 100 mole% ethylene was utilized as the feedstock to the gas phase polymerization; and (c) the dried product was admixed with 900 ppm of Lupersol 101.

10 The results are presented in Table I.

Comparative Example 5:

20 The procedure set forth above in Example 1 was repeated in its entirety except for the following changes: (a) 466 mg of the 30 wt% white oil slurry of the catalyst was utilized; (b) a gaseous flow of 100 mole% ethylene was utilized as the feedstock to the gas phase polymerization; and (c) no Lupersol 101 was added to the dried product.

25 The results are presented in Table I.

Comparative Example 6:

30 The procedure set forth above in Example 1 was repeated in its entirety except for the following changes: (a) 0.17 MPa g (25 psig) hydrogen was introduced into the liquid phase polymerization; (b) 350 mg of the 30 wt% white oil slurry of the catalyst was utilized; (c) a gaseous flow of 100 mole% ethylene was utilized as the feedstock to the gas phase polymerization; and (d) no Lupersol 101 was added to the dried product.

35 The results are presented in Table I.

Comparative Example 7:

40 The procedure set forth above in Example 1 was repeated in its entirety except for the following changes: (a) 0.17 MPa (25 psig) of hydrogen was introduced into the liquid phase polymerization; (b) 350 mg of the 30wt% white oil slurry of the catalyst was utilized; (c) the reactor was pressurized to 0.34 MPa g (50 psig) with hydrogen for five minutes, and then released, prior to the ethylene addition to terminate, by chain transfer, any remaining polymer chains on the living catalyst; and (d) the dried product was admixed with 1280 ppm of Lupersol 101.

45 The results are presented in Table I.

40 Table I set forth below includes synthesis conditions relating to whether utilization was made of polypropylene, and/or hydrogen in the ethylene polymerization phase and hydrogen in the propylene polymerization phase or peroxide visbreaking to set the product MFR. To facilitate mathematical analysis, utilizing multiple linear regression techniques, as described in "Applied Regression Analysis" (by N. R. Draper and H. Smith, John Wiley & Sons, Inc., N.Y. (1981)), these synthesis conditions are suitably coded as follows:

45 (a) -1 = 0 mole% propylene in feed to gas phase polymerization;
 +1 = 29 mole% propylene in feed to gas phase polymerization
 (b) -1 = 0 mole % hydrogen in feed to gas phase polymerization
 +1 = ca. 3 mole % hydrogen in feed to gas phase polymerization
 (c) -1 = no peroxide visbreaking of product
 50 +1 = peroxide visbreaking of product
 (d) -1 = no hydrogen in propylene polymerization
 +1 = hydrogen present in propylene polymerization
 (e) Measured by differential scanning calorimetry

55 The data from Examples 1-5 and Comparative Examples 1-6 were used in the mathematical analysis to generate the results shown in Tables II and III.

TABLE I

Example No.	MFR	Flex.Mod. 20% Secant	RTNI	Gard. Impact @ -18°C	C3-PE (a)	H2/PE (b)	R202 CR (c)	H2/PP (d)	Melt. Pt. PE, °C (e)
1	8.0	113.0	1.2	15	-1	-1	+1	-1	122.4
2	24.3	88.7	1.8	99	+1	-1	+1	-1	110.0
C 1	2.1	151.9	1.3	43	-1	-1	-1	+1	126.3
C 2	3.6	139.7	1.9	69	+1	-1	+1	-1	118.4
3	26.2	149.4	0.7	12	-1	+1	+1	-1	125.3
4	20.0	95.2	1.1	39	+1	+1	+1	-1	116.6
C 3	4.6	170.3	0.9	16	-1	+1	-1	+1	126.5
C 4	5.2	158.5	1.4	39	+1	+1	-1	+1	119.7
5	0.6	138.9	-	134	-1	-1	+1	-1	128.1
C 5	0.8	154.8	-	137	-1	-1	-1	-1	130.9
C 6	9.1	159.1	-	50	-1	-1	+1	+1	130.0
C 7	6.6	180.9	0.9	8	-1	-1	+1	+1	128.8

Table II

5	Dependent Variable: Gardner			
10	Intercept = 111.326393			
	<u>VARIABLE</u>	<u>COEFFICIENT</u>	<u>1 SIGMA</u>	<u>TSTAT (5 D.F.)</u>
15	C3/PE	18.830253	11.1301561	1.69182289
	H2/PE	-13.7565781	11.4827041	-1.198026
	CR	18.9819282	11.7099279	1.62101153
	C3 PE*CR	13.04563	10.5989862	1.23083753
20	LOG(MFR)	-30.1264343	11.003636	-2.73786178
	R Squared = .747678721			
	F(5.5) = 2.96320123			

Table III

25	Dependent variable: Flex Mod.			
30	Intercept = 135.165517			
	<u>VARIABLE</u>	<u>COEFFICIENT</u>	<u>1 SIGMA</u>	<u>TSTAT(6 D.F.)</u>
35	C3/PE	-14.6405173	2.77945076	-5.2674138
	H2/PE	8.18448275	2.77945076	2.94464032
	CR	-20.9431035	2.72092945	-7.69704024
	C3 PE*CR	-7.63189656	2.72092945	-2.80488587
40	R Squared = .939490752			
45	F(4.6) = 23.3895991			

Considering the regression on the dependent variable of Gardner impact strength, the positive coefficients for the synthesis variables of propylene in the gas phase polymerization and visbreaking of the product show that each of these have a marked positive effect on Gardner impact. It should also be noted that a large positive term appears for the product of the above two variables so that their use, in combination, is particularly desirable. The negative coefficients for the synthesis variables of hydrogen in the gas phase polymerization and log(MFR) show that the highest impact strength obtains when a high molecular weight polyethylene is produced and when the MFR of the final composite product is as low as possible.

In general, regression on the dependent variable of flexural modulus shows the reverse dependence on the synthesis variables, i.e., the higher the impact, the lower the flexural modulus. An exception is that the flexural modulus is indicated to be independent of the MFR.

The melting point data on the polyethylene phase of the composition tends to substantiate the fact that graft molecules are formed in the visbreaking steps. In each case, the visbroken material has a reduced polyethylene melting point relative to the non-visbroken counterpart. This reduced melting point implies improved compatibility and intermixing at phase boundaries, made possible by the increasing concentration of grafted molecules in the visbroken case.

Also, the amount of melting point depression is greatest with high molecular weight propylene copolymerized polyethylene. This result probably derives because each radical combination event produces a greater weight of graft when the polyethylene macroradical is very high molecular weight itself. More grafting for the propylene copolymerized polyethylene derives because of the increased propensity of tertiary-hydrogens to free radical abstraction so that more sites for grafting by combination become available in this case.

The coefficients from the regressions can be used to estimate the properties of products not included in the set analyzed. For instance, the expected properties of Comparative Example 7 can be calculated. Results of this calculation predict the following vs. the found properties:

Comparative Example 7-Predicted vs Actual
Properties

Predicted Gardner	56	5
Impact @ -18°C:		
Actual Gardner Impact	8	
@ -18°C :		
Predicted Flexural	128.3	
Modulus :		
Actual Flexural	180.9	10
Modulus :		

The poor predictive power of the expressions for Comparative Example 7 clearly show that this material is from another population set. This result shows that it is important in operation of the invention to avoid termination of growing chains in the interval between the homopolymerization of propylene and the gas phase (co)polymerization of the ethylene if optimal impact strength is to be obtained. That is, mere physical blends, as opposed to reactor blends, are outside the scope of this invention. The result also indicates that products of the invention could not be obtained by simple blending of the ingredients whether the product is visbroken or not.

The predictive equations can also be utilized to compare properties of a set of the subject materials at equal melt flow rates. For instance, in Table IV the calculated moduli and Gardner impact strengths are shown for a common 5 MFR.

Table IV
Calculated Properties of Selected Materials Corrected to 5 MFR

Condition	C3 in PE	H2 in PE	Visbreak product	Flex. Mod.	Gardner@ -18 C	
1 no	yes	no		145,000	37	30
2 no	no	no		128,000	64	
3 yes	yes	no		100,000	99	
4 yes	no	no		84,000	127	
5 no	yes	yes		171,000	25	35
6 no	no	yes		155,000	52	
7 yes	yes	yes		157,000	35	
8 yes	no	yes		141,000	63	
Sum Gard for:	yes = 324	yes = 196	yes = 327			40
	no = 178	no = 306	no = 175			

This set of calculated results represents the eight vertices of a cube in three dimensional experimental space. Because the set is balanced, the sum of the vertices on a side versus the sum of the vertices on the opposite side allows qualitative evaluation of the effect of the selected control variable on the response variables while mixing the non-selected control variables. The sums for this qualitative evaluation are shown in Table IV.

It is clear from the above treatment that optimization of the product impact strength requires addition of propylene in the polyethylene synthesis step, production of a relatively high molecular weight polyethylene phase material, and a melt phase treatment of the composite product with a free radical source. These results are consistent with a process wherein polymeric radicals produced by the free radical source terminate by radical combination to produce graft/block molecules which then function to assist in dispersion of the included polyethylene phase and also to assure adequate adhesion between the matrix and included phases.

It is contemplated that utilization of methods for generating free radicals other than by utilization of peroxides will produce impact-modified polypropylene materials having substantially similar physical properties as those exemplified above, more particularly materials within the above-described mathematically-derived population set. Furthermore, it is contemplated that free radical decomposable olefins and free radical crosslinkable thermoplastic olefin other than those exemplified above, such as polypropylene and polyethylene thermoplastic materials, particularly as described herein, will produce useful impact-modified polypropylene materials as well.

The compositions of this invention may include stabilizers and additives conventionally employed in similar polyolefin compositions, such as antioxidants, stabilizers against actinic radiation, antistatic additives, crystallinity nucleating agents, pigments and mineral fillers.

The compositions of this invention are useful for automobile trim parts, battery containers, appliance parts and the like and, particularly, due to the compatibility characteristics described above, for multilayered plastic

articles such as bottles and food trays and the like.

Claims

5

1. Visbroken reactor blend of a free radical decomposable olefin polymer and a free radical crosslinkable thermoplastic olefin polymer.

2. Visbroken reactor blend of claim 1 wherein said free radical decomposable olefin polymer is present in an amount of at least 70 wt.% based on the total weight of the reactor blend.

10

3. Visbroken reactor blend of claim 1 or 2, wherein said free radical decomposable olefin polymer is polypropylene.

4. Visbroken reactor blend of claim 3 wherein said polypropylene is homopolypropylene.

5. Visbroken reactor blend of claim 3 wherein said polypropylene is a propylene copolymer having at least about 90 wt.% propylene.

15

6. Visbroken reactor blend according to any of claims 3 to 5, wherein said polypropylene prior to visbreaking has an MFR less than 1.0 dg/min, preferably less than 0.5 dg/min, and especially less than 0.2 dg/min.

20

7. Visbroken reactor blend according to any of the preceding claims wherein said free radical crosslinkable thermoplastic olefin polymer is present in an amount of from 5 to 30 wt.% based on the total weight of the reactor blend.

8. Visbroken reactor blend according to any of the preceding claims wherein said free radical crosslinkable thermoplastic olefin polymer is a thermoplastic polyethylene material.

9. Visbroken reactor blend of claim 8 wherein said polyethylene is a homopolymer of ethylene.

25

10. Visbroken reactor blend of claim 8 wherein said thermoplastic polyethylene material is an ethylene copolymer.

11. Visbroken reactor blend of claim 10 wherein said ethylene copolymer is a copolymer of ethylene with minor amounts of one or more other comonomers selected from C₃-C₁₀ alpha-olefins.

12. Visbroken reactor blend according to any of the preceding claims having a Melt Flow Rate in the range of 8.0 to 26.2.

30

13. Visbroken reactor blend according to any of the preceding claims having Gardner Impact strength at -18°C in the range of 15 to 134.

14. Process for preparing impact-modified polymeric material comprising:

(i) preparing a reactor blend of a free radical decomposable olefin polymer and a free radical crosslinkable thermoplastic olefin polymer;

(ii) visbreaking said reactor blend; and

(iii) recovering the product of said visbroken reactor blend.

35

15. Process of Claim 12 wherein said impact-modified polymeric material is Impact-modified polypropylene material, said reactor blend being prepared by:

(i) polymerizing propylene in the presence of a titanium-containing alpha-olefin polymerization catalyst to produce a first polymer;

(ii) polymerizing ethylene in the presence of the first polymer and the titanium-containing catalyst to produce a reactor blend of the first polymer and a thermoplastic ethylene polymer.

40

16. Process of claim 12 or 13, wherein step (i) is conducted in the essential absence of chain terminating agents.

45

17. The use of a visbroken reactor blend according to any of claims 1 to 11 as an impact modified polymer for example in automobile trim parts, battery containers, appliance parts, bottles or food trays.

50

55

60

65



Europäisches Patentamt
European Patent Office
Office européen des brevets



⑪ Publication number:

0 351 208 A3

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 89307073.0

⑮ Int. Cl.5: C08F 8/50, C08L 23/02

⑯ Date of filing: 12.07.89

⑭ Priority: 15.07.88 US 219681

⑰ Applicant: EXXON CHEMICAL PATENTS INC.

⑮ Date of publication of application:
17.01.90 Bulletin 90/03

200 Park Avenue
Florham Park New Jersey 07932(US)

⑯ Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

⑱ Inventor: Randall, James Carlton

⑰ Date of deferred publication of the search report:
10.06.92 Bulletin 92/24

Marnixlaan 64

B-1900 Overijse(BE)

Inventor: Huff, Terence

5101 Inverness

Baytown Texas 77521(US)

⑲ Representative: Dew, Melvyn John et al
Exxon Chemical Limited Exxon Chemical
Technology Centre P.O. Box 1
Abingdon Oxfordshire, OX13 6BB(GB)

④ Impact modified polymers.

⑤ Impact-modified polymeric materials are produced by visbreaking certain reactor blends. In a preferred embodiment, impact-modified polypropylene materials are produced by visbreaking a reactor blend of polypropylene and thermoplastic polyethylene. The polypropylene material is preferably homopolypropylene having a melt flow rate of less than about 1 dg/min. Such impact-modified polymeric materials manifest unexpected compatibility characteristics, increased impact resistance at low temperatures, improved antiblush characteristics and improved flow characteristics.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 7073

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. CL.5)	
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	C08F8/50 C08L23/02	
X	EP-A-0 208 330 (IDEMITSU) * page 2, line 18 - page 3, line 6 * * page 3, line 22 - page 4, line 1 * * page 6, line 6 - page 7, line 11 * * page 11, line 23 - page 12, line 7 * * page 12, line 15 - page 13, line 6 * —	1-8, 10, 12, 14-17	C08K C08F C08L	
Y	US-A-3 629 368 (J. FUKUDA ET AL) * column 2, line 26 - line 36 * —	1-17	TECHNICAL FIELDS SEARCHED (Int. CL.5)	
Y	US-A-4 061 694 (E.G. CASTAGNA) * column 2, line 35 - line 54 * * column 3, line 1 - line 39 * * column 4, line 4 - line 10 * * column 5, line 9 - line 63 * —	1-17		
Y	US-A-4 489 034 (S. DAVISON) * column 2, line 1 - line 44 * * column 3, line 19 - line 45 * * column 4, line 34 - line 39 * * column 5, line 40 - line 50 * * table I * —	1-17		
D, Y	US-A-4 375 531 (J. F. ROSS) * column 3, line 10 - line 33 * * column 3, line 53 - line 65 * —	1-17		
A	EP-A-0 208 353 (AKZO) * column 3, line 35 - column 5, line 47 * —	1-12		
The present search report has been drawn up for all claims				
Place of search	Date of completion of the search	Examiner		
THE HAGUE	07 APRIL 1992	SCHMIDT H. R.		
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document		
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document				